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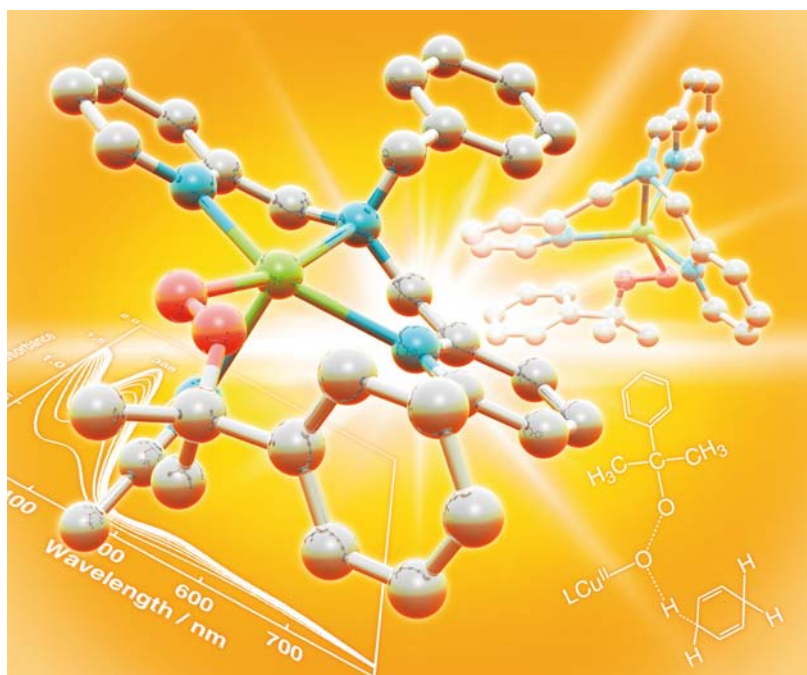


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PAPER

New nickel(II) and iron(II) helicates and tetrahedra derived from expanded quaterpyridines†

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As an extension of prior studies involving the linear quaterpyridine ligand, 5,5'''-dimethyl-2,2':5',5'':2'', 2'''-quaterpyridine **1**, the synthesis of the related expanded quaterpyridine derivatives **2** and **3** incorporating dimethoxy-substituted 1,4-phenylene and tetramethoxy-substituted 4,4'-biphenylene bridges between pairs of 2,2'-bipyridyl groups has been carried out *via* double-Suzuki coupling reactions between 5-bromo-5'-methyl-2'-bipyridine and the appropriate di-pinacol-diboronate esters using microwave heating. Reaction of **2** and **3** with selected Fe(II) or Ni(II) salts yields a mixture of both $[M_2L_3]^{4+}$ triple helicates and $[M_4L_6]^{8+}$ tetrahedra, in particular cases the ratio of the products formed was shown to be dependent on the reaction conditions; the respective products are all sufficiently inert to allow their chromatographic separation and isolation. Longer reaction times and higher concentrations were found to favour tetrahedron formation. The X-ray structures of solvated $[Ni_2(2)_3](PF_6)_4$, $[(PF_6)_6 \subset Fe_4(2)_6](PF_6)_7$, $[Fe_4(3)_6](PF_6)_8$ and $[Ni_4(3)_6](PF_6)_8$ have been determined, while the structure of the parent Fe(II) cage in the series, $[(PF_6)_6 \subset Fe_4(1)_6](PF_6)_7$, was reported previously. The internal volumes of the Fe(II) tetrahedral cages have been calculated and increase from 102 Å³ for $[Fe_4(1)_6]^{8+}$ to 227 Å³ for $[Fe_4(2)_6]^{8+}$ to 417 Å³ for $[Fe_4(3)_6]^{8+}$ and to an impressive 839 Å³ for $[Ni_4(3)_6]^{8+}$. The corresponding void volume in the triple helicate $[Ni_2(2)_3]^{4+}$ is 29 Å³.

Introduction

Considerable interest continues to be given to the metal-ion directed assembly of metallosupramolecular systems that enclose a central cavity – especially when the latter displays host–guest chemistry.^{1–3} However, the design and synthesis of such multi-component assemblies showing predefined properties continues to offer a considerable challenge. Typically the strategy employed involves the selection of ligand(s) and metal(s) displaying appropriate electronic and steric properties that will act in concert to promote formation of the required assembly. Like many others, we have employed such an approach for the synthesis of a range of discrete structures incorporating 2- and 3-dimensional voids, many of which were demonstrated to include guest molecules or ions.^{4–7}

More recently, we have focused our attention on the metal-directed assembly of such discrete systems exhibiting increased size and/or structural complexity.^{8–12} Clearly an approach for achieving larger systems is to increase the size of the organic component(s) employed. Nevertheless, it is noted that as individual components become larger they also tend to become more flexible and multiple products, often in equilibrium, may result; sometimes these exhibit similar component ratios. Thus, when essentially linear ligand systems are involved, M_3L_3 triangles are frequently formed along with M_4L_4 squares, or M_2L_3 helices with M_4L_6 tetrahedra.^{13–15} Hence, the balance between flexibility and rigidity of the (typically) di- or polytopic ligands employed in self-assembly processes can be an important factor in achieving a particular supramolecular architecture.^{16,17} Clearly, in this context the choice of metal ion is also important. For example, in previous studies, it was shown that the near-rigid, linear ditopic ligand, 5,5'''-dimethyl-2,2':5',5'':2'', 2'''-quaterpyridine **1**, yields $[Fe_4L_6]^{8+}$ tetrahedra when reacted with a range of Fe(II) salts (often spontaneously including an anion in the central cavity of the tetrahedral cage).^{4,5} However, with this ligand the slightly larger and more kinetically inert Ru(II) forms a $[Ru_2L_3]^{4+}$ triple helicate under the conditions employed.¹³

As an extension of the above studies, we now report the results of a comparative investigation of the effect of extending the structure of quaterpyridine **1** on the nature of the metallo-supramolecular assemblies formed with selected Fe(II) and Ni(II) salts. In the present study we have synthesised the extended quaterpyridine

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† Electronic supplementary information (ESI) available: further details of the NMR, UV/vis, fluorescence studies and cage void representations and organic precursor synthesis for selected systems. CCDC reference numbers 822504–822507. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1dt10667h

ligands, **2** and **3**, respectively incorporating methoxy-substituted phenyl and biphenyl bridges between the bipyridyl metal-binding domains of **1**. It was of particular interest to probe what effect the inherent additional flexibility of the extended ligand systems **2** and **3** might have on the corresponding metallocsupramolecular systems generated (Fig. 1).

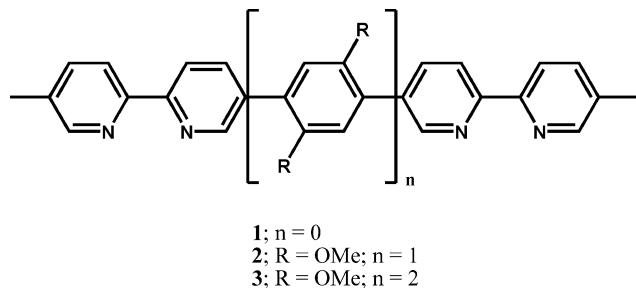


Fig. 1 The quaterpyridine ligands, **2** and **3** synthesised as part of the present study.

Results and discussion

Quaterpyridine ligand synthesis

The syntheses of expanded quaterpyridine **2** in 83% and its further expanded analogue **3** in 95% yield were conducted using microwave driven¹⁸ bis-Suzuki couplings of bipyridine with the boronic esters, 1,4'-Bis-(4,4,5,5-tetramethyl[1,3,2]dioxaborolan)-2,5-dimethoxybenzene and 4,4'-bis-(4,4,5,5-tetramethyl[1,3,2]dioxaborolan)-1,1'-(2,2',5,5'-tetramethoxy)biphenyl, respectively.¹⁹ The ¹H and ¹³C NMR spectra of both **2** and **3** were consistent with the expected two fold symmetry for these products. Signals for the 2,2'-bipyridyl moieties of each compound were assigned using NOESY and COSY measurements. As expected, the assignment of shifts corresponding to the dimethoxyphenylene bridge of **2** was straightforward, with one aromatic singlet ($\delta = 7.07$ ppm) and one methoxy singlet ($\delta = 3.86$ ppm) being evident. However, the presence of closely spaced peaks for the different aromatic and methoxy protons on the tetramethoxybiphenylene-bridge of **3** made full assignment of its ¹H NMR spectrum difficult. The HRMS data for both **2** and **3** were both in accord with the proposed structures.

[M₂L₃]⁴⁺ helicates and [M₄L₆]⁸⁺ tetrahedra

In an initial experiment, microwave heating of Fe(BF₄)₂·6H₂O and **2** in acetonitrile in a pressurised microwave vessel resulted in a red solution; thin layer chromatography (TLC) of this solution showed that a mixture of two deep red products was present. The ¹H NMR spectrum of the mixture was in accord with the two fold symmetry of quaterpyridine **2** being retained in each case and indicated that a 1:2 ratio of the two species was formed under the reaction conditions employed. Subsequent column chromatography on silica gel using previously reported conditions²⁰ resulted in their efficient separation. The deep red colour of each compound was in keeping with the presence of a low-spin *d*⁶ [Fe(bipyridine)₃]²⁺ chromophore in each case.²¹ The respective ¹H NMR and ¹³C NMR spectra of the separated products in CD₃CN once again confirmed that **2** exhibited C₂ symmetry in each species (8 ¹H and

15 ¹³C resonances were present). The ESI-HRMS of the higher *R_f* product showed +2, +3, and +4 ions corresponding to successive losses of PF₆[−] from the formula Fe₂(**2**)₃(PF₆)₄, while that for the lower *R_f* material gave +3, +4, and +5 ions corresponding to successive losses of PF₆[−] from the formula Fe₄(**2**)₆(PF₆)₈. Thus the MS and NMR data (see ESI) are in accord with the formulation of these products as [Fe₂(**2**)₃](PF₆)₄ and [Fe₄(**2**)₆](PF₆)₈, respectively – with the possibility that the latter complex might encapsulate an anion, as occurs in [(PF₆)₄ ⊂ Fe₄(**1**)₆](PF₆)₇,⁵ not able to be ruled out.

In subsequent experiments in which the microwave reaction time was lengthened and/or the concentration of the reactants increased it was observed that the reaction was driven towards the sole formation of [Fe₄(**2**)₆](PF₆)₈, in agreement with the [Fe₄(**2**)₆]⁸⁺ cation being the thermodynamic product. The ¹⁹F NMR spectrum of [Fe₄(**2**)₆](PF₆)₈ in CD₃CN gave a single resonance for the PF₆[−] counterions – indicating the presence of a single environment with respect to the NMR time scale. Thus the spectrum is not diagnostic for anion inclusion in the cationic tetrahedral cage (if inclusion were to occur, exchange in and out of the cage was anticipated to be fast given the expected larger size of both the cavity and the faces of the [Fe₄(**2**)₆]⁸⁺ cation relative to those of [Fe₄(**1**)₆]⁸⁺ for which slow PF₆[−] exchange was observed).⁵

No crystals of [Fe₂(**2**)₃](PF₆)₄ suitable for X-ray crystallography were obtained. However, reaction of **2** with Ni(II) resulted in yellow crystals that were suitable. The resulting crystal structure revealed the formation of a dinuclear triple helicate of type [Ni₂(**2**)₃](PF₆)₄ with its two octahedral Ni(II) centres separated by 11.8 Å and bridged by three quaterpyridine ligands (Fig. 2). The helicate crystallises in the hexagonal chiral space group *P*6₃22 with one third of the complex in the asymmetric unit; the stereochemistry of the metal centres in each discrete helix is either $\Delta\Delta$ (*P*) or $\Lambda\Lambda$ (*M*) and each crystal is itself optically active. The chiral twist of the helicate extends the entire length of the molecule and equates to 66°. Despite full conjugation the ligands are not flat but are bent 35° from an idealised planar form. The central dimethoxyphenylene rings are twisted such that they are orientated about the centre of the helix to form an enclosed void-space, the volume of which was calculated by Voidoo²² to be 29 Å³ (Fig. 2).

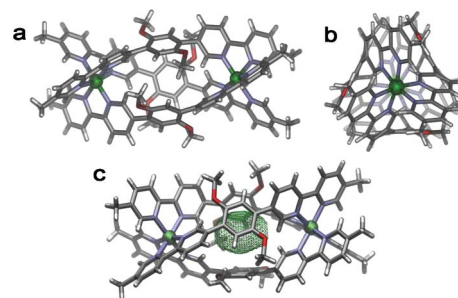


Fig. 2 a) Crystal structure of [Ni₂(**2**)₃](PF₆)₄ viewed perpendicular to its C₃-axis; b) view down the C₃-axis showing the helical twist and c) with Voidoo²² calculated void volume shown as a green mesh.

Crystals of [Fe₄(**2**)₆](PF₆)₈ suitable for X-ray diffraction were grown from tetrahydrofuran/acetonitrile and the resulting structure confirmed the formation of a tetrahedral assembly (Fig. 3a and 3b). Interestingly, a PF₆[−] anion (disordered over two positions) and a quarter occupancy acetonitrile solvent molecule are

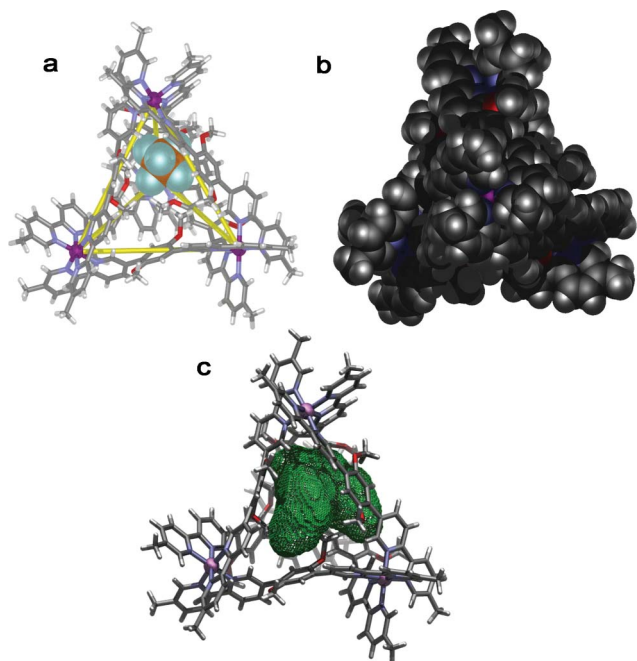


Fig. 3 Representations of the crystal structure of $[\text{Fe}_4(\mathbf{2})_6 \supset \text{PF}_6](\text{PF}_6)_7$; a) illustrates the encapsulated PF_6^- guest, b) is a space filling diagram viewed down a C_3 -axis and c) shows the void volume of the cage (green mesh) as calculated by Voidoo;²² counterions, solvent and disorder are removed for clarity.

encapsulated within the cage such that the solid state formula is $[\{(\text{PF}_6)(\text{MeCN})_{0.25}\} \subset \text{Fe}_4(\mathbf{2})_6] \cdot 7\text{PF}_6 \cdot 2.75 \text{ MeCN} \cdot 9.35\text{H}_2\text{O}$. The product crystallises $P\bar{1}$ and individual $\text{Fe}(\text{II})$ centres in each tetrahedron contain homochiral metal centres; that is, each tetrahedron is either $AAAA$ or $AAAA$ rendering the cage T -symmetric. Each of the ligands (which bridge metals of the same handedness) are arranged such that the chelating groups are orientated mutually *anti* to each other. The chiral twist associated with each $[\text{Fe}_4(\mathbf{2})_6]^{8+}$ tetrahedron is evident when viewed down one of the C_3 -axes (Fig. 3b); the ligands are twisted some 20° from an idealised planar *anti*-configuration. The average distance between each of the $\text{Fe}(\text{II})$ centres is 13.43 \AA , which is significantly longer than the 9.45 \AA observed in the crystal structures of $[\text{Fe}_4(\mathbf{1})_6]^{8+}$ reported previously.⁵ As calculated by Voidoo²² the void volume of the small tetrahedral cation, $[\text{Fe}_4(\mathbf{1})_6]^{8+}$ (see ESI†), is 102 \AA^3 , similar to that reported for other similarly sized tetrahedra while that for the larger tetrahedron incorporating $\mathbf{2}$ now reported is increased to 227 \AA^3 . Interestingly, this calculated volume is lower than that calculated if the encapsulated volume is considered a tetrahedron with edge length equal to the metal–metal distance (285 \AA^3). This in part reflects the twisted orientations of the dimethoxyphenylene rings, with the methoxy groups intruding into the cavity reducing the encapsulated volume somewhat.

The most noticeable difference in the UV-vis spectra of $[\text{Fe}_4(\mathbf{2})_6](\text{PF}_6)_8$ and $[\text{Fe}_2(\mathbf{2})_3](\text{PF}_6)_4$ (see ESI†) is that the MLCT band for the former (386 nm) shows a small shift relative to the latter (374 nm). The fluorescence spectrum of $[\text{Fe}_2(\mathbf{2})_3](\text{PF}_6)_4$ in acetonitrile (see ESI†) revealed a strong emission at 450 nm (blue) and a weaker emission at 736 nm resulting from excitation of this complex at 374 nm . Similarly, a strong emission at

455 nm and a weaker emission at 761 nm were observed when $[\text{Fe}_4(\mathbf{2})_6](\text{PF}_6)_8$ was irradiated at 386 nm . The higher energy emissions of both complexes are strongly concentration dependent in agreement with the presence of intermolecular quenching and thus there is the possibility that aggregation behaviour may occur in solution. Clearly the photophysical characteristics suggest potential applications;^{23,24} for example, for fluorescent signalling of a host–guest interaction for use in a guest-specific sensor.²⁵ In this context we have already demonstrated that $[\text{Fe}_4(\mathbf{1})_6]^{8+}$ discriminates between particular anions.⁵

In a parallel synthesis to that of $[\text{Fe}_2(\mathbf{2})_3](\text{PF}_6)_4$, reaction of the tetramethoxybiphenylene quaterpyridine $\mathbf{3}$ with $\text{Fe}(\text{II})$ resulted in the generation of both $[\text{Fe}_2(\mathbf{3})_3](\text{PF}_6)_4$ and $[\text{Fe}_4(\mathbf{3})_6](\text{PF}_6)_8$ as products in an approximate $1 : 9$ ratio respectively (based on the NMR spectrum of the initial crude product). In subsequent syntheses the individual assemblies were isolated following chromatography on silica gel. The mass spectrum of $[\text{Fe}_2(\mathbf{3})_3](\text{PF}_6)_4$ gave $+3$ and $+4$ ions consistent with the successive losses of PF_6^- from the above formula. At 300 K the ^1H NMR spectrum of this product showed five relatively sharp aromatic signals corresponding to pyridyl protons in the 3- and 4-positions together with the phenylene protons in the 6,6'-positions. Three broad aromatic peaks corresponding to pyridyl protons in the 6''-positions and biphenylene protons in the 3,3'-positions were also present (see ESI†). This suggested the presence of a dynamic process on the NMR timescale. Variable temperature ^1H NMR measurements over a limited temperature range resulted in a clear change in the spectrum: at 290 K the broad peaks observed at ambient temperature are further broadened, whilst at 310 K the peaks begin to sharpen; some minor signal shifts were also observed. However, in the absence of further data it is inappropriate to speculate further about the origins of this behaviour. As for $[\text{Fe}_2(\mathbf{2})_3]^{4+}$ and $[\text{Fe}_4(\mathbf{2})_6]^{8+}$, $[\text{Fe}_2(\mathbf{3})_3]^{4+}$ and $[\text{Fe}_4(\mathbf{3})_6]^{8+}$ can be separated chromatographically; however, in this case the dinuclear species, $[\text{Fe}_2(\mathbf{3})_3]^{4+}$, in acetonitrile was observed to undergo partial conversion to $[\text{Fe}_4(\mathbf{3})_6]^{8+}$ over a three day period. Once again, the evidence suggests that the tetrahedral cage $[\text{Fe}_4(\mathbf{3})_6]^{8+}$ is the thermodynamically favoured product.

In contrast to the ^1H NMR spectrum of $[\text{Fe}_2(\mathbf{3})_3](\text{PF}_6)_4$, $[\text{Fe}_4(\mathbf{3})_6](\text{PF}_6)_8$ gave a sharp spectrum with the expected 11 ^1H and 19 ^{13}C resonances, indicating again that $\mathbf{3}$ exhibits C_2 -symmetry within the complex. As before, protons in the 6''- and 6'''-positions give resonances that were shifted upfield relative to those of the free ligand (see ESI†). This product is stable in solution for months, consistent with it being favoured thermodynamically. The mass spectrum showed $+3$ to $+7$ ions corresponding to successive losses of PF_6^- from the formula $[\text{Fe}_4(\mathbf{3})_6](\text{PF}_6)_8$.

The red colour of both $[\text{Fe}_2(\mathbf{3})_3](\text{PF}_6)_4$ and $[\text{Fe}_4(\mathbf{3})_6](\text{PF}_6)_8$ once again suggested the presence of a $[\text{Fe}(\text{bipyridine})_3]^{2+}$ chromophore.²¹ The UV-vis and fluorescence properties of $[\text{Fe}_2(\mathbf{3})_3](\text{PF}_6)_4$ and $[\text{Fe}_4(\mathbf{3})_6](\text{PF}_6)_8$ parallel those described for $[\text{Fe}_2(\mathbf{2})_3](\text{PF}_6)_4$ and $[\text{Fe}_4(\mathbf{2})_6](\text{PF}_6)_8$. Each shows a MLCT band at $\sim 530 \text{ nm}$. The most noticeable differences in the UV-vis spectra are the CT ($\pi-\pi^*$) bands associated with the presence of the tetramethoxybiphenylene bridge; there is a small blue shift for $[\text{Fe}_2(\mathbf{3})_3](\text{PF}_6)_4$ (365 nm) relative to the corresponding absorption for $[\text{Fe}_4(\mathbf{3})_6](\text{PF}_6)_8$ (376 nm) (see ESI†). Fluorescence spectroscopy revealed a strong emission (blue) at 451 nm and a weaker emission at 719 nm resulting from excitation of $[\text{Fe}_2(\mathbf{3})_3](\text{PF}_6)_4$ at 365 nm .

Similarly a strong emission at 453 nm and a weaker emission at 743 nm were observed when $[\text{Fe}_4(\mathbf{3})_6](\text{PF}_6)_8$ was irradiated at 376 nm (see ESI†). As for the corresponding complexes of **2**, the higher energy emissions for both complexes are strongly concentration dependent²⁶ in keeping with the occurrence of intermolecular quenching and possible concomitant aggregation behaviour.

Crystals of $[\text{Fe}_4(\mathbf{3})_6](\text{PF}_6)_8$ suitable for X-ray diffraction were grown from THF/ CH_3CN and the resulting structure once again confirmed the presence of a tetrahedral assembly (Fig. 4). The product crystallises in the centric tetragonal space group $I4_1/a$ and is situated around a $\bar{4}$ special position. In contrast to the tetrahedra so far discussed, in the X-ray structure there are no encapsulated guest molecules. Each tetrahedron possesses two Δ and two Λ metal centres resulting in idealised S_4 symmetry. Interestingly, the ^1H NMR of this material (see earlier) indicated that this is not the case in the solution where the spectrum is in accord with a T -symmetric isomer exclusively. Perhaps this indicates the presence of a level of fast equilibration in solution with respect to the NMR timescale. However, reported rates^{27–29} for the racemisation reaction of $[\text{Fe}_2(2,2'\text{-bipyridine})_3]^{2+}$ (using a range of experimental conditions) are slow in comparison to the NMR timescale. Hence fast racemisation at the metal centres seems unlikely, particularly since M_4L_6 systems related to the current system are reported to result in much slower rates of racemisation than their mononuclear counterparts.³⁰ Alternatively, the preferential crystallisation of the $AAAA$ stereoisomer following a slow isomerisation from either $AAAA$ or $AAAA$ -stereoisomers may occur. Related solution/crystallisation behaviour has been observed in similar sized cage molecules.^{7,9} Reflecting the S_4 symmetry of $[\text{Fe}_4(\mathbf{3})_6]^{8+}$, and in contrast to the T -symmetric complexes $[\text{Fe}_4(\mathbf{1})_6]^{8+}$ and $[\text{Fe}_4(\mathbf{2})_6]^{8+}$, there are two ligand arrangements present. The bipyridine domains in two individual ligands adopt approximate *anti* arrangements (linking metal centres of the same chirality), with the remaining four ligands exhibiting near *syn* arrangements (linking metal centres of opposite chirality)^{7,9,30}

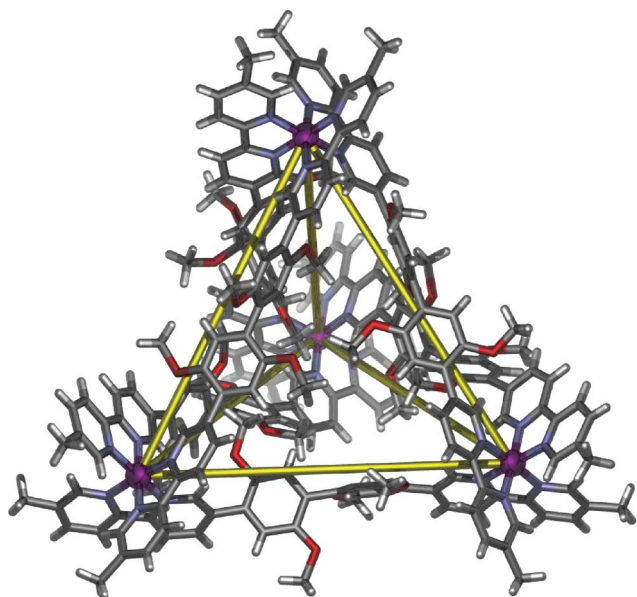


Fig. 4 X-ray structure of $[\text{Fe}_4(\mathbf{3})_6](\text{PF}_6)_8 \cdot 12.5\text{THF}$.

The chelating moieties of each ligand are approximately planar. The average Fe–Fe distance is 16.9 Å, which corresponds to a substantial Voidoo²² calculated cavity volume of approximately 417 Å³, which again is smaller than 570 Å³ encapsulated by the metal–metal tetrahedron.

The possibility that $[\text{Fe}_4(\mathbf{3})_6]^{8+}$ may encapsulate a BPh_4^- anion was also probed. BPh_4^- has a volume of 368 Å³,³¹ which corresponds to a fill ratio of 44% for the T -symmetric $[\text{M}_4(\mathbf{3})_6]^{8+}$ species (see below). Based on related species, such a ratio suggested that BPh_4^- would be a suitable guest.^{1,9,32} From inspection of the crystal structure of $[\text{Fe}_4(\mathbf{3})_6]^{8+}$, paying particular attention to the size of the faces, it seems likely that a BPh_4^- anion would be able to undergo a ‘through side’ exchange process (assuming some flexibility in the bound ligand structures).³³ ^1H NMR experiments to investigate this possibility were undertaken. One equivalent of BPh_4^- was added to a solution of $[\text{Fe}_4(\mathbf{3})_6](\text{BF}_4)_8$ in CD_3CN and the changes in the spectrum compared (see ESI†). Significant broadening of the 6,6'-proton and the 2,2'-methoxy-proton signals were observed and the possibility that dynamic behaviour was present was probed using variable temperature NMR. As the temperature was lowered further broadening occurred until at 280 K the above-mentioned peaks were almost obscured; increasing the temperature to 340 K led to a sharpening of these peaks. This behaviour is consistent with an anion exchange process occurring on the NMR timescale. Further evidence for possible BPh_4^- encapsulation came from a fluorescence study. One equivalent of BPh_4^- was added to an acetonitrile solution of $[\text{Fe}_4(\mathbf{3})_6](\text{BF}_4)_8$ and comparison of the fluorescence emission spectra of this and the starting solution on irradiation at 376 nm revealed a large increase in emission intensity at 453 nm for the former coupled with a decrease at 742 nm (ESI†). This enhancement of the higher energy emission may possibly be related to partial desolvation of the $[\text{Fe}_4(\mathbf{3})_6]^{8+}$ cavity through inclusion of BPh_4^- , leading to a subsequent reduction in solvent mediated quenching.²⁴ However such a proposal is, of course, not unequivocal.

Interestingly, an analogous metal-directed assembly of **3** using $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in place of $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$, yielded a solid product whose ESI-HRMS revealed the presence of both $[\text{Ni}_2\text{L}_3]^{4+}$ and $[\text{Ni}_4\text{L}_6]^{8+}$ assemblies. Recrystallisation from an acetonitrile/methanol/tetrahydrofuran mixture, however, yielded single crystals of $\{(\text{H}_2\text{O})_{0.5}(\text{THF})_{0.75}(\text{MeCN})_{0.5}\} \subset \text{Ni}_4(\mathbf{3})_6(\text{PF}_6)_8 \cdot 5.5\text{MeCN} \cdot 5\text{THF} \cdot \text{MeOH} \cdot 4.075\text{H}_2\text{O}$ suitable for X-ray diffraction. The structure revealed, in contrast to $[\text{Fe}_4(\mathbf{3})_6](\text{PF}_6)_8$, that a T -symmetric homochiral tetrahedron resulted. Once again, like $[\text{Fe}_4(\mathbf{1})_6](\text{PF}_6)_8$ and $[\text{Fe}_4(\mathbf{2})_6](\text{PF}_6)_8$, each tetrahedron corresponds to either a $AAAA$ - $[\text{Ni}_4(\mathbf{3})_6](\text{PF}_6)_8$ or a $AAAA$ - $[\text{Ni}_4(\mathbf{3})_6](\text{PF}_6)_8$ entity (Fig. 5) with the average Ni–Ni distance being 17.4 Å. As with other homochiral tetrahedra, each of the ligands is arranged with its chelating moieties in an approximate *anti* orientation and the bipyridine groups are not co-planar, with a twist from planarity of 22° being observed. The Voidoo¹ calculated volume of this species is 839 Å³ placing it amongst the largest encapsulated volumes reported for such a complex.^{1,9,15} This volume is almost twice that calculated for $[\text{Fe}_4(\mathbf{3})_6](\text{PF}_6)_8$ which reflects both the higher symmetry of the cage (resulting in longer M–M distances), the presence of guest solvent molecules, and a more open structure with the methoxy groups aligned closer to the faces of the tetrahedron. This substantial difference in volume also indicates the flexibility of the cage

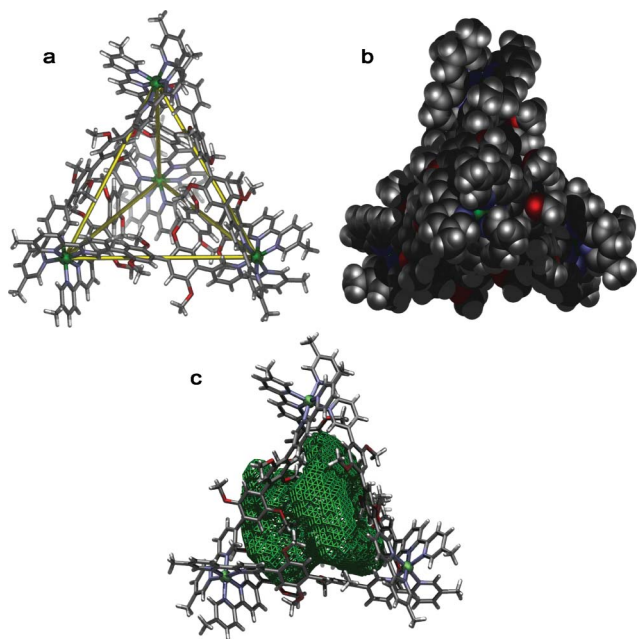


Fig. 5 a) The crystal structure of $[\text{Ni}_4(\mathbf{3})_6](\text{PF}_6)_8$, b) a space filling representation and c) the void volume in the cage (green mesh) as calculated by Voidoo;²² counterions, solvent and disorder are removed for clarity.

system^{15,33} and hence reinforces the observations concerning anion binding discussed above.

Finally, a comparison of the structures of the cations in $[\text{Fe}_4(\mathbf{3})_6](\text{PF}_6)_8$ and $[\text{Ni}_4(\mathbf{3})_6](\text{PF}_6)_8$ viewed perpendicular to a C_3 -axis illustrating the difference in the chiral arrangements at the metal centres is presented in Fig. 6.

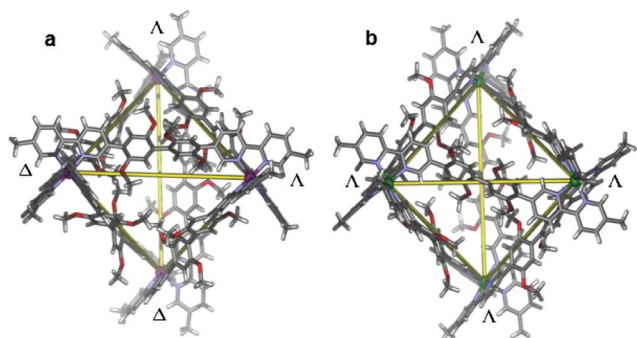


Fig. 6 Comparative views of the X-ray crystal structures of a) $[\text{Fe}_4(\mathbf{3})_6](\text{PF}_6)_8$ and b) $[\text{Ni}_4(\mathbf{3})_6](\text{PF}_6)_8$ viewed perpendicular to a C_3 -axis; $[\text{Fe}_4(\mathbf{3})_6](\text{PF}_6)_8$ has S_4 symmetry; *anti*-ligands bridge metals of the same chirality, *syn*-ligands bridge metals of opposite handedness; $[\text{Ni}_4(\mathbf{3})_6](\text{PF}_6)_8$ has T symmetry; *anti*-ligands bridge all metals as it is homochiral; hydrogens, counterions and solvent are removed for clarity.

Concluding remarks

In this report we have demonstrated that the interaction of the extended quaterpyridines **2** and **3** with octahedral Fe(II) or Ni(II) metal ions resulted in mixtures of $[\text{M}_2\text{L}_3]^{4+}$ helicates and $[\text{M}_4\text{L}_6]^{8+}$ tetrahedra. A level of control over the relative ratio of these products was demonstrated using a variation of the reaction time and/or the degree of dilution employed for the synthesis.

Individual products have been isolated and in four cases their crystal structures determined. The calculated cavity volumes of the present series of Fe(II) and Ni(II) tetrahedral cages increase from 102 Å³ for $[\text{Fe}_4(\mathbf{1})_6]^{8+}$ to 227 Å³ for $[\text{Fe}_4(\mathbf{2})_6]^{8+}$ to 417 Å³ for $[\text{Fe}_4(\mathbf{3})_6]^{8+}$ and to an impressive 839 Å³ for $[\text{Ni}_4(\mathbf{3})_6]^{8+}$. Preliminary evidence suggests that the larger tetrahedral cages may display interesting host–guest chemistry and further studies to probe this aspect are planned for the future.

Experimental

NMR spectra were recorded on a Bruker AM-300 or a Varian Mercury 300 MHz spectrometer (300.133 MHz) at 298 K. Electrospray (ES) high resolution Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS) measurements on a Bruker BioAPEX 47e mass spectrometer equipped with an Analytica of Branford electrospray ionisation (ESI) source. The fluorescence spectrum was obtained on a Perkin Elmer LS55 spectrofluorimeter. 2-bromo-1,4-dimethoxybenzene,³⁴ 2-trimethylstannyl-5-methyl pyridine, 5-bromo-5'-methyl-2,2'-bipyridine³⁵ and 1,4-diiodo-2,5-dimethoxybenzene³⁶ were prepared by reported procedures. The boronic esters 1,4'-bis-(4,4,5,5-tetramethyl[1,3,2]dioxaborolan)-2,5-dimethoxybenzene and 4,4'-bis-(4,4,5,5-tetramethyl[1,3,2]dioxaborolan)-1,1'-(2,2',5,5'-tetramethoxy)biphenyl were prepared by a modification of a reported procedure³⁷ (see below) in which the more reactive *t*-butyllithium was employed in two-fold excess and reaction times were extended up to 3 h at −78 °C to ensure that bis-lithiation had occurred prior to treatment with 2-isopropoxy-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane. An additional comment on the synthesis of 4,4'-dibromo-2,5,2',5'-tetramethoxy-biphenyl is presented in the ESI.†

1,4'-Bis-(4,4,5,5-tetramethyl[1,3,2]dioxaborolan)-2,5-dimethoxybenzene

t-Butyllithium (9.4 cm³, 1.7 M in pentane, 16 mmol) was added dropwise to a stirred solution of 1,4-diiodo-2,5-dimethoxybenzene (1.56 g, 4 mmol) in dry tetrahydrofuran (30 cm³) at −78 °C. The reaction was stirred for a further 1 h at −78 °C and this was followed by the dropwise addition of 2-isopropoxy-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (2.98 g, 16 mmol). The reaction mixture was allowed to warm to room temperature and stirred overnight. After removal of the tetrahydrofuran under vacuum, H₂O (30 cm³) was added and the pH adjusted to 8 using 1 M HCl. The product was extracted with Et₂O (2 × 30 cm³) and the combined organic phases washed with brine and dried over Na₂SO₄. The solvent was removed under vacuum and the crude material purified by recrystallisation from petrol affording the product (1.17 g, 80%) as white microcrystals. ¹H NMR (300 MHz, CDCl₃): δ = 1.36 (s, 24 H, CH₃), 3.75 (s, 6 H, OCH₃), 7.05 (s, 2 H, H-3,6); ¹³C NMR (75 MHz, CDCl₃): δ = 25.05, 57.17, 83.81, 119.03, 158.27.

2,5,2',5'-Tetramethoxybiphenyl

A suspension of $[\text{NiCl}_2(\text{PPh}_3)_2]$ (4.38 g, 7 mmol), zinc metal (1.96 g, 30 mmol) and tetraethylammonium iodide (5.66 g, 22 mmol) in dry tetrahydrofuran (50 cm³) was degassed with N₂ for 0.5 h. This solution was then stirred until a deep maroon colour developed

(–0.5 h). To this was added a nitrogen purged tetrahydrofuran (10 cm³) solution of 2-bromo-1,4-dimethoxybenzene (4.34 g, 20 mmol) and the reaction mixture was heated at 50 °C for 20 h. On cooling to room temperature, 5 M NH₃ (50 cm³) was added and the resulting reaction mixture stirred overnight. Ethyl acetate (40 cm³) was added and the mixture was filtered through celite. The organic phase was isolated and the aqueous layer was extracted with ethyl acetate (40 cm³). The organic fractions were combined and extracted with 4 M HCl (3 × 40 cm³). The aqueous layer was neutralised with NaOH pellets, extracted with dichloromethane (3 × 40 cm³) and the dichloromethane extracts dried over Na₂SO₄. The solvent was removed under vacuum and the solid that remained was purified by chromatography on silica gel with a 2:1 mixture of petrol: dichloromethane as eluent to afford the product (1.92 g, 70%) as a white crystalline solid. ¹H NMR (300 MHz, CDCl₃): δ = 3.74 (s, 6 H, OCH₃), 3.79 (s, 6 H, OCH₃), 6.84–6.95 (m, 6 H, H-3,3',4,4',6,6').

4,4'-Dibromo-2,5,2',5'-tetramethoxy-biphenyl

A stirred solution of 2,5,2',5'-tetramethoxybiphenyl (1.70 g, 6.2 mmol) and *N*-bromosuccinimide (3.31 g, 18.6 mmol) in dichloromethane (30 cm³) was refluxed for 10 h. The resulting reaction mixture was washed with H₂O and the organic layer dried over Na₂SO₄. The crude material was purified by chromatography on silica gel with a 1:1 mixture of dichloromethane/petrol as eluent to afford the product (2.57 g, 96%) as a white crystalline solid. ¹H NMR (300 MHz, CDCl₃): δ = 3.74 (s, 6 H, OCH₃), 3.86 (s, 6 H, OCH₃), 6.83 (s, 2 H, H-6,6'), 7.18 (s, 2 H, H-3,3'); ¹³C NMR (75 MHz, CDCl₃): δ = 56.79, 57.10, 111.17, 115.42, 117.06, 126.85, 150.06, 151.42.

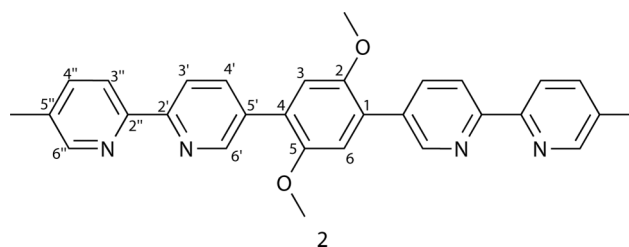
4,4'-Bis-(4,4,5,5-tetramethyl[1,3,2]dioxaborolan)-1,1'-(2,2',5,5'-tetramethoxy)biphenyl

The procedure was as for the synthesis of 1,4'-bis-(4,4,5,5-tetramethyl[1,3,2]dioxaborolan)-2,5-dimethoxybenzene but using 4,4'-dibromo-2,5,2',5'-tetramethoxybiphenyl (1.3 g, 3 mmol), *t*-butyllithium (7 cm³, 1.7 M in pentane, 12 mmol) and 2-isopropoxy-4,4,5,5-tetramethyl[1,3,2]dioxaborolane (2.23 g, 12 mmol) in tetrahydrofuran (30 cm³). The tetrahydrofuran was removed under vacuum followed by the addition of H₂O. This mixture was neutralised with 2 M HCl and then extracted with dichloromethane (2 × 50 cm³). The combined organic fractions were dried over Na₂SO₄. The dichloromethane was removed and the solid that remained recrystallised from petrol to afford the product (1.1 g, 70%) as white microcrystals. ¹H NMR (300 MHz, CDCl₃): δ = 1.36 (s, 24 H, CH₃), 3.75 (s, 6 H, OCH₃), 3.79 (s, 6 H, OCH₃), 6.80 (s, 2 H, H-6,6'), 7.30 (s, 2 H, H-3,3'); ¹³C NMR (75 MHz, CDCl₃): δ = 25.05, 56.87, 57.12, 83.69, 114.88, 119.83, 132.03, 150.95, 158.60.

1,4-Bis[5'-(5'''-methyl-2',2''-bipyridyl)]-2,5-dimethoxybenzene (2)

A solution of 5-bromo-5'-methyl-2,2'-bipyridine (1.49 g, 6 mmol), 1,4'-bis-(4,4,5,5-tetramethyl[1,3,2]dioxaborolan)-2,5-dimethoxybenzene (1.00 g, 2.7 mmol) and K₂CO₃ (2.50 g, 18 mmol, in 5 cm³ of H₂O) in DMF (15 cm³) was degassed with N₂. Pd(PPh₃)₄ (208 mg, 0.18 mmol) was added to this solution and the reaction mixture was heated with microwave energy in a

sealed pressurised microwave vessel with temperature and pressure sensors and a magnetic stirrer bar (Step 1 – the temperature was ramped to 120 °C over 2 min using 100% of 400 W; Step 2 – the solution was held at 120 °C for 8–20 min using 30% of 400 W). H₂O (20 cm³) was added and the resulting precipitate was isolated by filtration. Recrystallisation of the crude product from methanol afforded **2** (1.06 g, 83%) as pale yellow microcrystals. ¹H NMR (300 MHz, CDCl₃): δ = 2.42 (s, 6 H, CH₃), 3.86 (s, 6 H, OCH₃), 7.07 (s, 2 H, H-3,6), 7.67 (dd, ³*J* = 8.1 Hz, ⁴*J* = 1.8 Hz, 2 H, H-4''), 8.07 (dd, ³*J* = 8.1 Hz, ⁴*J* = 2.1 Hz, 2 H, H-4'), 8.36 (d, ³*J* = 8.1 Hz, 2 H, H-3''), 8.46 (d, ³*J* = 8.1 Hz, 2 H, H-3'); 8.55 (d, ⁴*J* = 1.8 Hz, 2 H, H-6''), 8.91 (d, ⁴*J* = 2.1 Hz, 2 H, H-6') (Scheme 1); ¹³C NMR (75 MHz, CDCl₃): δ = 18.64, 56.67, 114.47, 120.29, 120.45, 120.93, 127.51, 127.74, 133.77, 137.91, 149.64, 149.77, 151.32, 153.46, 154.74; positive ion ESI-HRMS: *m/z* (*M* = C₃₀H₂₇N₄O₂; in dichloromethane/methanol): calcd for [*M* + H]⁺: 475.2134, found 475.2124; calcd for [*M* + Na]⁺: 497.1954, found 497.1940.



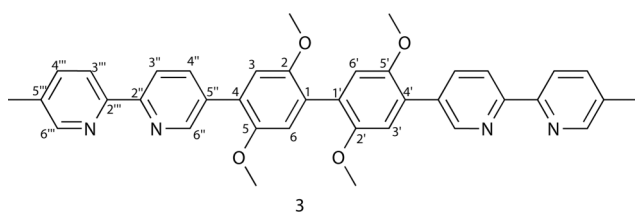
Scheme 1 The numbering scheme used for the assignment of the ¹H NMR resonances in **2**.

4,4'-Bis[5'-(5'''-methyl-2',2''-bipyridyl)]-(2,2',5,5'-tetramethoxy)biphenyl (3)

The procedure was as for the synthesis of **2** but using 5-bromo-5'-methyl-2,2'-bipyridine (277 mg, 1.11 mmol), 4,4'-bis-(4,4,5,5-tetramethyl[1,3,2]dioxaborolan)-1,1'-(2,2',5,5'-tetramethoxy)biphenyl (263 mg, 0.5 mmol), K₂CO₃ (460 mg, 3.33 mmol) and Pd(PPh₃)₄ (38 mg, 0.03 mmol) in DMF (7 cm³). After standard workup the crude product was purified by chromatography on silica gel with dichloromethane (97.5%), methanol (2%) and saturated aqueous NH₃ (0.5%) as eluent to afford the product (260 mg, 95%) as an off-white solid. ¹H NMR (300 MHz, CDCl₃): δ = 2.41 (s, 6 H, CH₃), 3.82 (s, 6 H, 2,2' or 5,5'-OCH₃), 3.85 (s, 6 H, 2,2' or 5,5'-OCH₃), 7.03 (s, 2 H, H-3,3' or 6,6'), 7.06 (s, 2 H, H-3,3' or 6,6'), 7.69 (dd, ³*J* = 8.1 Hz, ⁴*J* = 1.5 Hz, 2 H, H-4''), 8.09 (dd, ³*J* = 8.3 Hz, ⁴*J* = 2.1 Hz, 2 H, H-4'), 8.38 (d, ³*J* = 8.1 Hz, 2 H, H-3''), 8.48 (d, ³*J* = 8.3 Hz, 2 H, H-3''), 8.54 (d, ⁴*J* = 1.5 Hz, 2 H, H-6''), 8.94 (d, ⁴*J* = 2.1 Hz, 2 H, H-6') (Scheme 2); ¹³C NMR (75 MHz, CDCl₃): δ = 18.60, 56.53, 56.85, 114.19, 115.50, 120.62, 121.09, 126.83, 128.16, 133.87, 134.30, 138.20, 149.45, 149.54, 150.71, 151.52, 153.06, 153.96; positive ion ESI-HRMS: *m/z* (*M* = C₃₈H₃₄N₄O₄; in dichloromethane/methanol): calcd for [*M* + H]⁺: 611.2653, found 611.2623; calcd for [*M* + Na]⁺: 633.2472, found 633.2467.

[Fe₂(2)₃](PF₆)₄

A mixture of Fe(BF₄)₂·6H₂O (24 mg, 0.07 mmol) and **2** (50 mg, 0.105 mmol) in acetonitrile (50 cm³) was heated in a sealed pressurised microwave vessel with temperature and pressure sensors and a magnetic stirrer bar (Step 1 – ramped to 130 °C over 2 min



Scheme 2 The numbering scheme used for the assignment of the ^1H NMR resonances in **3**.

using 100% of 400 W; Step 2 – held at 130 °C for 10 min using 25% of 400 W). The crude product was purified by chromatography on silica gel with acetonitrile, water and saturated KNO_3 (7 : 1 : 0.5) as eluent. The first of the two observed red bands to be eluted was collected. The purified product (49 mg, 70%) was isolated as a red solid by precipitation with excess aqueous NH_4PF_6 in water (20 cm^3) followed by filtration. UV/Vis (acetonitrile, nm): λ_{max} ($\epsilon \text{ dm}^{-3} \text{ mol}^{-1} \text{ cm}^{-1}$) = 263 (50 360), 318 (138 000), 374 (75 370), 537 (13 190); ^1H NMR (300 MHz, CD_3CN): δ = 2.28 (s, 18 H, CH_3), 3.49 (s, 18 H, OCH_3), 6.78 (s, 6 H, H-3,6), 7.23 (d, 4J = 1.2 Hz, 6 H, H-6'), 7.30 (d, 4J = 1.2 Hz, 6 H, H-6''), 8.01 (dd, 3J = 8.1 Hz, 4J = 1.2 Hz, 6 H, H-4'), 8.39 (dd, 3J = 8.4 Hz, 4J = 1.2 Hz, 6 H, H-4''); 8.50 (d, 3J = 8.1 Hz, 6 H, H-3'), 8.91 (d, 3J = 8.4 Hz, 6 H, H-3''); ^{13}C NMR (75 MHz, CD_3CN): δ = 19.09, 58.22, 116.80, 124.60, 124.89, 126.13, 137.22, 137.37, 139.88, 140.52, 151.21, 154.53, 156.02, 157.02, 159.58; positive ion ESI-HRMS: m/z ($M = \text{C}_{90}\text{H}_{78}\text{P}_4\text{F}_{24}\text{Fe}_2\text{N}_{12}\text{O}_6$; in acetonitrile/methanol): calcd for $[M - 2\text{PF}_6]^{2+}$: 912.7086, found 912.7042; calcd for $[M - 3\text{PF}_6]^{3+}$: 560.1508, found 560.1490; calcd for $[M - 4\text{PF}_6]^{4+}$: 383.8719, found 383.8708.

$[\text{Fe}_4(2)_6](\text{PF}_6)_8$

A mixture of $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (24 mg, 0.07 mmol) and **2** (50 mg, 0.105 mmol) in acetonitrile (10 cm^3) was heated in a sealed pressurised microwave vessel with temperature and pressure sensors and a magnetic stirrer bar (Step 1 – ramped to 130 °C over 2 min using 100% of 400 W; Step 2 – held at 130 °C for 30 min using 25% of 400 W). The crude product was purified by chromatography on silica gel with acetonitrile, water and saturated KNO_3 (7 : 1 : 0.5) as eluent. The second of the two observed red bands to be eluted was collected. The purified product was isolated by precipitation with excess aqueous NH_3PF_6 in water (20 cm^3) followed by filtration to yield the product (68 mg, 96%) as a red solid. UV/Vis (acetonitrile, nm): λ_{max} ($\epsilon \text{ dm}^{-3} \text{ mol}^{-1} \text{ cm}^{-1}$) = 256 (94, 410), 318 (266 840), 386 (157 450), 535 (27 420); ^1H NMR (300 MHz, CD_3CN): δ = 2.19 (s, 36 H, CH_3), 3.35 (s, 36 H, OCH_3), 6.86 (s, 12 H, H-3,6), 7.12 (d, 4J = 1.2 Hz, 12 H, H-6'), 7.94 (dd, 3J = 8.4 Hz, 4J = 1.2 Hz, 12 H, H-4'), 8.02 (d, 4J = 1.8 Hz, 12 H, H-6''), 8.31 (dd, 3J = 8.7 Hz, 4J = 1.8 Hz, 12 H, H-4''); 8.50 (d, 3J = 8.4 Hz, 12 H, H-3'), 8.57 (d, 3J = 8.7 Hz, 12 H, H-3''); ^{13}C NMR (75 MHz, CD_3CN): δ = 18.91, 57.45, 114.87, 124.28, 124.50, 125.91, 136.27, 139.09, 139.62, 140.45, 151.99, 155.25, 155.38, 157.16, 158.89; ^{19}F NMR (282.4 MHz, CD_3CN): δ = -73.28 (d, 1J = 706.8 Hz, 48 F, 8PF_6); positive ion ESI-HRMS: m/z ($M = \text{C}_{180}\text{H}_{156}\text{P}_8\text{F}_{48}\text{Fe}_4\text{N}_{24}\text{O}_{12}$ in acetonitrile/methanol): calcd for $[M - 3\text{PF}_6]^{3+}$: 1264.9324, found 1264.9310; calcd for $[M - 4\text{PF}_6]^{4+}$: 912.4581, found 912.4574; calcd for $[M - 5\text{PF}_6]^{5+}$: 700.9736, found 700.9731. Found: C, 49.85; H, 3.94; N, 7.35%. Calc. for $\text{C}_{180}\text{H}_{156}\text{P}_8\text{F}_{48}\text{Fe}_4\text{N}_{24}\text{O}_{12} \cdot 6\text{H}_2\text{O}$: C, 49.80;

H, 3.90; N, 7.75%. X-ray quality crystals were obtained by slow diffusion of methanol into an acetonitrile solution of the above product.

$[\text{Ni}_2(2)_3](\text{PF}_6)_4 \cdot 2\text{H}_2\text{O}$

A mixture of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (13.3 mg, 0.056 mmol) and **2** (40 mg, 0.084 mmol) in methanol (10 cm^3) was heated in a sealed pressurised microwave vessel with temperature and pressure sensors and a magnetic stirrer bar (Step 1 – ramped to 130 °C over 2 min using 100% of 400 W; Step 2 – held at 130 °C for 20 min using 25% of 400 W). Excess NH_4PF_6 in water (20 cm^3) was then added and the resulting solid isolated by filtration in near quantitative yield. This crude product gave MS evidence for the presence of the corresponding dinuclear complex, $[\text{Ni}_4(2)_6](\text{PF}_6)_8$. Positive ion ESI-HRMS: m/z ($M = \text{C}_{180}\text{H}_{156}\text{P}_8\text{F}_{48}\text{Ni}_4\text{N}_{12}\text{O}_6$; in acetonitrile/methanol): calcd for $[M - 3\text{PF}_6]^{3+}$: 1268.5984, found 1268.5931. This material was recrystallised by diffusion of tetrahydrofuran into an acetonitrile solution to afford the product (48 mg, 39%) as yellow crystals. Found: C, 50.14; H, 3.95; N, 7.89%. Calc. for $\text{C}_{90}\text{H}_{78}\text{P}_4\text{F}_{24}\text{Ni}_2\text{N}_{12}\text{O}_6 \cdot 2\text{H}_2\text{O}$: C, 50.13; H, 3.84; N, 7.80. Positive ion ESI-HRMS: m/z ($M = \text{C}_{90}\text{H}_{78}\text{P}_4\text{F}_{24}\text{Ni}_2\text{N}_{12}$; in acetonitrile/methanol): calcd for $[M - 2\text{PF}_6]^{2+}$: 915.2073, found 915.2093.

It is noted that the spectrum also gave evidence for the presence of the corresponding $[\text{Ni}_4\text{L}_6]^{8+}$ species – apparently generated under the conditions employed for the HRMS determination.

X-Ray quality crystals were obtained by slow diffusion of tetrahydrofuran into an acetonitrile solution of the above product.

$[\text{Fe}_2(3)_3](\text{PF}_6)_4$

A mixture of $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (7.4 mg, 0.022 mmol) and **3** (20 mg, 0.033 mmol) in acetonitrile (50 cm^3) was heated in a sealed pressurised microwave vessel with temperature and pressure sensors and a magnetic stirrer bar (Step 1 – ramped to 130 °C over 2 min using 100% of 400 W; Step 2 – held at 130 °C for 10 min using 25% of 400 W). The crude product was purified by chromatography on silica gel with acetonitrile, water and saturated KNO_3 (7 : 1 : 0.5) as eluent. The second of the two observed red bands to be eluted was collected. The purified product was isolated by precipitation with excess aqueous NH_4PF_6 in water (20 cm^3) followed by filtration, to afford the product (17 mg, 62%) as a red solid. UV/Vis (acetonitrile, nm): λ_{max} ($\epsilon \text{ dm}^{-3} \text{ mol}^{-1} \text{ cm}^{-1}$) = 267 (40 156), 307 (100 390), 365 (60 387), 532 (9555); ^1H NMR (300 MHz, CD_3CN): δ = 2.29 (s, 18 H, CH_3), 2.82 (br s, 18 H, OCH_3), 3.56 (s, 18 H, OCH_3), 6.59 (br s, 6 H), 7.00 (br s, 6 H), 7.15 (s, 6 H), 7.84 (br s, 6 H), 8.02 (dd, 3J = 8.1 Hz, 4J = 1.2 Hz, 6 H), 8.36 (dd, 3J = 8.4 Hz, 4J = 1.8 Hz, 6 H), 8.51 (d, 3J = 8.1 Hz), 8.61 (d, 3J = 8.4 Hz, 6 H). Positive ion ESI-HRMS: m/z ($M = \text{C}_{114}\text{H}_{102}\text{P}_4\text{F}_{24}\text{Fe}_2\text{N}_{12}\text{O}_{12}$; in acetonitrile/methanol): calcd for $[M - 3\text{PF}_6]^{3+}$: 696.2033, found 696.2033; calcd for $[M - 4\text{PF}_6]^{4+}$: 485.9113, found 485.9084.

$[\text{Fe}_4(3)_6](\text{PF}_6)_8$

A mixture of $\text{FeCl}_2 \cdot 5\text{H}_2\text{O}$ (12 mg, 0.055 mmol) and **3** (50 mg, 0.082 mmol) in methanol (10 cm^3) was heated with microwave energy in a sealed pressurised microwave vessel with temperature and pressure sensors and a magnetic stirrer bar (Step 1 – ramped

to 130 °C over 2 min using 100% of 400 W; Step 2 – held at 130 °C for 20 min using 25% of 400 W). The crude product was purified by chromatography on silica gel with acetonitrile, water and saturated KNO₃ (7 : 1 : 0.5) as eluent. The second of the two observed red bands to be eluted was collected. The purified product was isolated by precipitation with excess aqueous NH₄PF₆ in water (20 cm³) followed by filtration, to afford the product (62 mg, 90%) as a red solid. UV/Vis (acetonitrile, nm): $\lambda_{\text{max}}(\epsilon \text{ dm}^{-3} \text{ mol}^{-1} \text{ cm}^{-1}) = 271$ (114 304), 306 (310 254), 376 (187 839), 529 (29 000); ¹H NMR (300 MHz, CD₃CN): $\delta = 2.24$ (s, 36 H, CH₃), 3.43 (s, 36 H, 2,2'-OCH₃), 3.57 (s, 36 H, 5,5'-OCH₃), 6.86 (s, 12 H, H-6,6'), 6.88 (s, 12 H, H-3,3'), 7.28 (s, 12 H, H-6''), 7.76 (d, ⁴*J* = 1.8 Hz, 12 H, H-6''), 8.01 (d, ³*J* = 8.1 Hz, 12 H, H-4'''), 8.33 (dd, ³*J* = 8.4 Hz, ⁴*J* = 1.8 Hz, 12 H, H-4''); 8.55 (d, ³*J* = 8.1 Hz, 12 H, H-3'''), 8.60 (d, ³*J* = 8.4 Hz, 12 H, H-3''); ¹³C NMR (75 MHz, CD₃CN): $\delta = 18.94, 56.97, 57.09, 114.47, 116.72, 123.81, 124.51, 124.72, 3.52, 137.42, 139.45, 139.83, 140.35, 150.79, 152.35, 155.13, 155.44, 157.40, 158.50$; ¹⁹F NMR (282.4 MHz, CD₃CN): $\delta = -73.49$ (d, ¹*J* = 706.1 Hz, 48 F, 8PF₆). Positive ion ESI-HRMS: *m/z* (*M* = C₂₂₈H₂₀₄P₈F₄₈Fe₄N₂₄O₂₄; in acetonitrile/methanol): calcd for [*M* – 3PF₆]³⁺: 1537.3716, found 1537.3467; calcd for [*M* – 4PF₆]⁴⁺: 1116.7875, found 1116.7867; calcd for [*M* – 5PF₆]⁵⁺: 864.4370, found 864.4375; calcd for [*M* – 6PF₆]⁶⁺: 696.2034, found 696.1976; calcd for [*M* – 7PF₆]⁷⁺: 576.0365, found 576.0365. Found: C, 52.99, H, 3.96, N, 6.46%. Calc. for C₂₂₈H₂₀₄P₈F₄₈Fe₄N₂₄O₂₄·7H₂O: C, 52.91; H, 4.25; N, 6.50%. X-ray quality crystals were obtained by diffusion of tetrahydrofuran into an acetonitrile solution of the product.

[Ni₄(3)₆](PF₆)₈

NiCl₂·6H₂O (5.2 mg, 0.022 mmol) and **3** (20 mg, 0.033 mmol) in methanol (10 cm³) were heated in a sealed pressurised microwave vessel with temperature and pressure sensors and a magnetic stirrer bar (Step 1: ramped to 130 °C over 2 min using 100% of 400 W; Step 2: held at 130 °C for 20 min using 25% of 400 W). Excess NH₄PF₆ in water (20 cm³) was then added and the resulting yellow solid isolated by filtration in near quantitative yield. This product before recrystallisation also gave MS evidence for the additional presence of [Ni₂(3)₃](PF₆)₄. Positive ion ESI-HRMS: *m/z* (*M* = C₁₁₄H₁₀₂P₄F₂₄Ni₂N₁₂O₁₂; in acetonitrile/methanol): calcd for [*M* – 2PF₆]²⁺: 1119.2866, found 1119.2896. The crude material was recrystallised by slow diffusion of tetrahydrofuran into an acetonitrile solution to afford (15 mg, 58%) as yellow cubic crystals. Positive ion ESI-HRMS: *m/z* (*M* = C₂₂₈H₂₀₄P₈F₄₈Ni₄N₂₄O₂₄; in acetonitrile/methanol): calcd for [*M* – 3PF₆]³⁺: 1541.0371, found 1541.0573. X-ray quality crystals were obtained by slow diffusion of tetrahydrofuran into an acetonitrile solution of the above product.

X-Ray studies

Data for [{(PF₆)(MeCN)_{0.25}}] ⊂ Fe₄(2)₆](PF₆)₇·2.75MeCN·9.35H₂O, [Ni₂(2)₃](PF₆)₄·2.5MeCN and [(H₂O)_{0.5}(THF)_{0.75}](MeCN)_{0.5}] ⊂ Ni₄(3)₆](PF₆)₈·5.5MeCN·5THF·MeOH·4.075H₂O were collected on a Bruker-Nonius APEX2-X8-FR591 diffractometer employing graphite-monochromated Mo-Kα radiation generated from a rotating anode (0.71073 Å) with ω and ψ scans to approximately 56° 2 θ at 150(2) K.³⁸ Data for [Fe₄(3)₆](PF₆)₈·12.5THF were collected at approximately 100 K using double diamond

monochromated synchrotron radiation (0.48595 Å) and ω and ψ scans at the ChemMatCARS beamline at the Advanced Photon Source. Data integration and reduction were undertaken with SAINT and XPREP.³⁹ Subsequent computations were carried out using the WinGX-32 graphical user interface.⁴⁰ Structures were solved by direct methods using SIR97.⁴¹ Multi-scan empirical absorption corrections, when applied, were applied to the data set using the program SADABS.⁴² Data were refined and extended with SHELXL-97 and SHELXH-97.⁴³ In general, non-hydrogen atoms with occupancies greater than 0.5 were refined anisotropically. Carbon-bound hydrogen atoms were included in idealised positions and refined using a riding model. Oxygen and nitrogen bound hydrogen atoms were first located in the difference Fourier map before refinement. Where these hydrogen atoms could not be located, they were not modelled. In all cases the crystals employed were extremely solvent sensitive and required rapid handling (~30 s) at low temperatures in order to facilitate data collection. Crystallographic data and specific details pertaining to structural refinements is summarised below.

[Ni₂(2)₃](PF₆)₄·2.5MeCN

Formula C₉₅H_{85.50}F₂₄N_{14.50}Ni₂O₆P₄, *M* 2223.58, hexagonal, space group *P*6₃(#173), *a* 13.460(2), *b* 13.460(2), *c* 30.805(5) Å, γ 120.00°, *V* 4833.3(12) Å³, *D*_c 1.528 g cm⁻³, *Z* 2, crystal size 0.150 × 0.10 × 0.05 mm, colour yellow, habit plate, temperature 150(2) K, $\lambda(\text{MoK}\alpha)$ 0.71073 Å, $\mu(\text{MoK}\alpha)$ 0.564 mm⁻¹, *T*(SADABS)_{min,max} 0.831645, 1.00000, $2\theta_{\text{max}}$ 50.00, *hkl* range –16 16, –15 16, –36 36, *N* 62378, *N*_{ind} 5653(*R*_{merge} 0.0458), *N*_{obs} 5090(*I* > 2σ(*I*)), *N*_{var} 438, residuals‡ *R*₁(*F*) 0.0878, *wR*₂(*F*²) 0.2395, GoF(all) 1.003, $\Delta\rho_{\text{min,max}}$ –1.526, 0.671 e– Å⁻³.

Specific details. The methoxy groups in the structure are disordered over two positions. The O(1) containing group was modelled over two unequal positions (occupancy 0.75 and 0.25), while the O(2) containing group was modelled in two equal occupancy positions. Each of the anions is disordered over special positions with several fluorine positions required for each and were included with identical thermal parameters. In addition, there is a large region of smeared electron density present in the lattice and despite several attempts at modelling this as solvent including the use of bond restraints and rigid-bodies no satisfactory model could be found. The SQUEEZE function of PLATON⁴⁴ was employed to remove this contribution from the model and it was included in the formula weight calculations as five acetonitrile solvent molecules per unit cell. The refined Flack parameter of 0.34(4) suggests that although each helix is chiral there was some racemic twinning present in the crystal employed.

[{(PF₆)(MeCN)_{0.25}}] ⊂ Fe₄(2)₆](PF₆)₇·2.75MeCN·9.35H₂O

Formula C₁₈₆H_{183.70}F₄₈Fe₄N₂₇O_{21.35}P₈, *M* 4522.06, triclinic, space group *P*1̄(#2), *a* 20.2470(12), *b* 20.7900(12), *c* 30.5460(17) Å, α 82.126(3), β 76.935(3), γ 73.436(3)°, *V* 11969.0(12) Å³, *D*_c 1.255 g cm⁻³, *Z* 2, crystal size 0.250 × 0.150 × 0.100 mm, colour red, habit prism, temperature 150(2) K, $\lambda(\text{MoK}\alpha)$ 0.71073 Å, $\mu(\text{MoK}\alpha)$

‡ *R*₁ = $\Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ for *F*_o > 2σ(*F*_o); *wR*₂ = $(\Sigma w(F_o^2 - F_c^2)^2 / \Sigma (w(F_c^2)^2))^{1/2}$ all reflections *w* = 1/[σ²(*F*_o²) + (0.1276*P*)² + 16.3939*P*] where *P* = (*F*_o² + 2*F*_c²)/3

0.387 mm⁻¹, $T(\text{SADABS})_{\text{min,max}}$ 0.744008, 1.00000, $2\theta_{\text{max}}$ 50.70, hkl range $-24\ 24, -25\ 25, -36\ 36$, N 280847, N_{ind} 43649 (R_{merge} 0.0424), N_{obs} 33936 ($I > 2\sigma(I)$), N_{var} 2760, residuals $\| R_1(F) 0.1192, wR_2(F^2) 0.3245, \text{GoF}(\text{all}) 1.384, \Delta\rho_{\text{min,max}} -1.173, 1.761 \text{ e-}\text{\AA}^{-3}$.

Specific details. There is a significant amount of disorder present in the structure. One of the central dimethoxyphenylene rings is disordered over two 50% occupancy positions, the anions are disordered over 11 positions with a total occupancy of 8, the acetonitriles over 7 positions and the water molecules over 38 positions. A number of restraints and constraints were required to facilitate realistic modelling in the phenylene ring and the disordered anions and where multiple fluorine positions were present they were modelled with identical thermal parameters. The water hydrogen atoms could not be located in the difference Fourier map and were not included in the final model.

$[\{(\text{H}_2\text{O})_{0.5}(\text{THF})_{0.75}(\text{MeCN})_{0.5}\} \subset \text{Ni}_4(3)_6(\text{PF}_6)_8 \cdot 5.5\text{MeCN} \cdot 5\text{THF} \cdot \text{MeOH} \cdot 4.075\text{H}_2\text{O}$

Formula $\text{C}_{264}\text{H}_{279.75}\text{F}_{48}\text{N}_{30}\text{Ni}_4\text{O}_{35.315}\text{P}_8$, M 5832.63, triclinic, space group $P\bar{1}(\#2)$, a 21.1588(12), b 24.2022(14), c 37.7344(22) Å, α 78.498(4), β 79.573(4), γ 76.780(3)°, V 18247.0(18) Å³, D_c 1.062 g cm⁻³, Z 2, crystal size 0.250 × 0.180 × 0.100 mm, colour yellow, habit block, temperature 150(2) K, $\lambda(\text{MoK}\alpha)$ 0.71073 Å, $\mu(\text{MoK}\alpha)$ 0.318 mm⁻¹, $T(\text{SADABS})_{\text{min,max}}$ 0.6737, 0.7457, $2\theta_{\text{max}}$ 50.00, hkl range $-25\ 24, -28\ 28, -44\ 44$, N 443400, N_{ind} 63078 (R_{merge} 0.0693), N_{obs} 39105 ($I > 2\sigma(I)$), N_{var} 3755, residuals $\| R_1(F) 0.1123, wR_2(F^2) 0.3001, \text{GoF}(\text{all}) 1.173, \Delta\rho_{\text{min,max}} -1.723, 4.107 \text{ e-}\text{\AA}^{-3}$.

Specific details. There is a significant amount of disorder present in the structure. The P(5)-containing anion is modelled as disordered over two equal occupancy positions and each of the methyl groups was modelled with disordered hydrogen atoms over two equal positions leading to some artificial close H–H contacts. The remaining solvent was successfully modelled as a number of both full and partial occupancy solvent molecules including THF, MeCN, MeOH and water. A number of bond length restraints were required to facilitate the realistic modelling of this solvent. The water hydrogen atoms could not be located in the difference Fourier map and were not included in the final model.

$[\text{Fe}_4(3)_6](\text{PF}_6)_8 \cdot 12.5\text{THF}$

Formula $\text{C}_{278}\text{H}_{304}\text{F}_{48}\text{Fe}_4\text{N}_{24}\text{O}_{36.50}\text{P}_8$, M 5948.61, tetragonal, space group $I41/a(\#88)$, a 42.764(2), b 42.764(2), c 17.3170(16) Å, V 31669(4) Å³, D_c 1.248 g cm⁻¹, Z 4, crystal size 0.10 × 0.070 × 0.05 mm, colour red, habit prism, temperature 100(2) K, $\lambda(\text{synchrotron})$ 0.49594 Å, $\mu(\text{synchrotron})$ 0.169 mm⁻¹, $2\theta_{\text{max}}$ 29.96, hkl range $-44\ 44, -38\ 44, -18\ 18$, N 34440, N_{ind} 7446 (R_{merge} 0.0609), N_{obs} 6161 ($I > 2\sigma(I)$), N_{var} 649, residuals $\| R_1(F) 0.1623, wR_2(F^2) 0.3879, \text{GoF}(\text{all}) 1.691, \Delta\rho_{\text{min,max}} -1.096, 1.010 \text{ e-}\text{\AA}^{-3}$.

$\| R_1 = \Sigma \|F_o\| - \|F_c\| / \Sigma \|F_o\|$ for $F_o > 2\sigma(F_o)$; $wR_2 = (\Sigma w(F_o^2 - F_c^2)^2 / \Sigma (w(F_c^2)^2))^{1/2}$ all reflections $w = 1/[\sigma^2(F_o^2) + (0.1000P)^2 + 50.5000P]$ where $P = (F_o^2 + 2F_c^2)/3$

$\| R_1 = \Sigma \|F_o\| - \|F_c\| / \Sigma \|F_o\|$ for $F_o > 2\sigma(F_o)$; $wR_2 = (\Sigma w(F_o^2 - F_c^2)^2 / \Sigma (w(F_c^2)^2))^{1/2}$ all reflections $w = 1/[\sigma^2(F_o^2) + (0.1000P)^2 + 68.0000P]$ where $P = (F_o^2 + 2F_c^2)/3$

$\| R_1 = \Sigma \|F_o\| - \|F_c\| / \Sigma \|F_o\|$ for $F_o > 2\sigma(F_o)$; $wR_2 = (\Sigma w(F_o^2 - F_c^2)^2 / \Sigma (w(F_c^2)^2))^{1/2}$ all reflections $w = 1/[\sigma^2(F_o^2) + (0.1500P)^2 + 100.0000P]$ where $P = (F_o^2 + 2F_c^2)/3$

Specific details. The crystals employed in this study were very small, diffracted poorly and rapidly suffered solvent loss. Despite the use of synchrotron radiation, rapid handling times and a low temperature collection no reflection data were observed at better than 1.0 Å resolution. In addition, the crystals appeared to decay further during data collection resulting in lower than ideal data completeness. Despite these limitations the data is of more than sufficient quality to unambiguously determine the connectivity of the structure. The P(2) and P(3) containing anions were each disordered and modelled over two equal occupancy positions and the methyl hydrogens were also all modelled as disordered over two equal positions. The C(13) containing dimethoxyphenylene ring was also modelled as disordered over two equal positions. While one 0.5 occupancy THF could be modelled in the lattice, the remaining solvent is significantly disordered and despite numerous attempts at modelling, including with multiple rigid bodies no satisfactory model for the electron-density associated with them could be found. Therefore the SQUEEZE function of PLATON⁴⁴ was employed to remove the contribution of the electron density associated with the anions from the model, which resulted in far more satisfactory residuals and was included in the formula weight calculations as 42 tetrahydrofuran solvent molecules per unit cell. Because of the use of synchrotron radiation no adsorption correction was applied.

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